Liquid Organic Hydrogen Carriers (LOHC): An auspicious alternative to conventional hydrogen storage technologies

J. von Wild, T. Friedrich, A. Cooper, B. Toseland, G. Muraro, W. TeGrotenhuis, Y. Wang, P. Humble, A. Karim

This document appeared in

Detlef Stolten, Thomas Grube (Eds.):
18th World Hydrogen Energy Conference 2010 - WHEC 2010
Parallel Sessions Book 4: Storage Systems / Policy Perspectives, Initiatives and Co-operations
Proceedings of the WHEC, May 16.-21. 2010, Essen
Schriften des Forschungszentrums Jülich / Energy & Environment, Vol. 78-4
Institute of Energy Research - Fuel Cells (IEF-3)
Forschungszentrum Jülich GmbH, Zentralbibliothek, Verlag, 2010
ISBN: 978-3-89336-654-5

Liquid Organic Hydrogen Carriers (LOHC): An auspicious alternative to conventional hydrogen storage technologies

J. von Wild, T. Friedrich, BMW Group Research and Technology, Germany
A. Cooper, B. Toseland, G. Muraro, Air Products & Chemicals
Ward TeGrotenhuis, Yong Wang, Paul Humble, Ayman Karim, Pacific Northwest National Laboratory, USA

1 Introduction

Due to the limited availability of fossil fuels – the finite nature and instability of fossil fuel supply and limited production rate – mankind is facing increasing pressure to establish a sustainable alternative energy economy. At least since the so-called “oil crises” in the 1970’s, the automotive industry has started to strive towards a possible substitution of an oil-based energy carrier. As the optimum long-term solution, hydrogen has been identified as an energy carrier, produced on the basis of renewable energy sources (water, sun, wind, biomass) and distributed and stored within adapted infrastructure with new or modified facilities for car refueling.

The realistic implementation of this vision, among others, has been pursued at BMW for more than 30 years in the framework of the “CleanEnergy” program [1]. The results that have been obtained are promising, showing the feasibility of that vision in principle. For instance, the BMW hydrogen record car H2R [2-4] has proven the performance of a hydrogen car powered by an internal combustion engine. The fleet of BMW Hydrogen 7 serial cars [5-7] persuasively demonstrated the suitability and durability for daily use. Another conclusion in the course of these 30 years: the costs to install a new and nationwide infrastructure of fueling stations for hydrogen distribution will be the biggest hurdle for a substantial implementation of the hydrogen economy in the automotive vehicle sector. This is due to the currently established methods of hydrogen storage in the form of cryogenic liquid or pressurized hydrogen. In this respect, it is worth thinking about alternative methods of hydrogen storage [8], which require less energy and cost efforts for distribution and vehicle storage.

2 Discussion

Looking at alternative ways of hydrogen storage for mobile applications, both the systems at fueling stations and onboard the vehicle must be considered concurrently. Thereby, the biggest technical challenge remains onboard the vehicle, as fuel systems in mobile systems have to be compact and lightweight to maintain the best driving dynamics and transportation performance. Additionally, a number of safety relevant criteria have to be fulfilled. Vehicle refueling has to be simple, fast and – last, but not least – affordable. Fulfilling of all these parameters is not an easy task considering the physical and chemical properties of hydrogen. Hydrogen is the element with the lowest specific volumetric density (ca. 84 g / m^3). Confining a lot of hydrogen in a small space is rather challenging. On the other hand, hydrogen possesses a very high gravimetric energy density of 120 kJ / g (lower heating value), which is three times higher than that of gasoline. For a mileage of 500 km, a medium-sized sedan needs 5 kg of hydrogen stored onboard the vehicle. The volumetric and gravimetric goal for a

suitable hydrogen storage system should remain under realistic considerations below 125 l und 100 kg, translating into a volumetric density of 40 g H_2 per liter system volume and a gravimetric storage density of 50 g H_2 per kg system mass (= 5 mass%).

A postulated power demand of such a car (with 100 kW nominal power) requires the supply of ca. 150 g / min. or 9 kg / hr. hydrogen, to be fulfilled by the storage system. Technologically, the most common (automotive) storage of hydrogen is in a physical way as cryogenic liquid and compressed gas. Cryogenic liquid hydrogen offers in combination with lightweight tanks built of aluminum or carbon fiber composite structures currently the greatest potential with respect to gravimetric and volumetric storage densities. The biggest disadvantage is the unavoidable loss of hydrogen due to evaporation of liquid hydrogen during longer stand-still periods. Compressed H_2 tanks require, at acceptable volumetric storage densities, very high storage pressure up to currently 700 bar. Increasing pressure compels more demanding requirements to the structural design of the (always cylindrical) tank. Promising are so-called cryo-compressed tank systems, where hydrogen is stored simultaneously under high pressures and cryogenic temperatures. BMW has developed such a cryo-compressed hydrogen storage concept, which is now undergoing a system and component validation to prove compliance with automotive requirements before it can be demonstrated in a BMW test vehicle [9]. All physical storage systems require a new fuelling station infrastructure, a topic which is currently elaborated in the German *H_2-Mobility* initiative.

Besides the above-mentioned physical storage, a variety of alternative storage methods exist. Alternative storage means the sorption of hydrogen, either chemically or physically, to an additional chemical element. Hydrogen is released from that chemical bonding through heating (thermolysis) or via a direct chemical reaction with additional reagents. Figure 1 shows a choice of the various existing storage technologies.

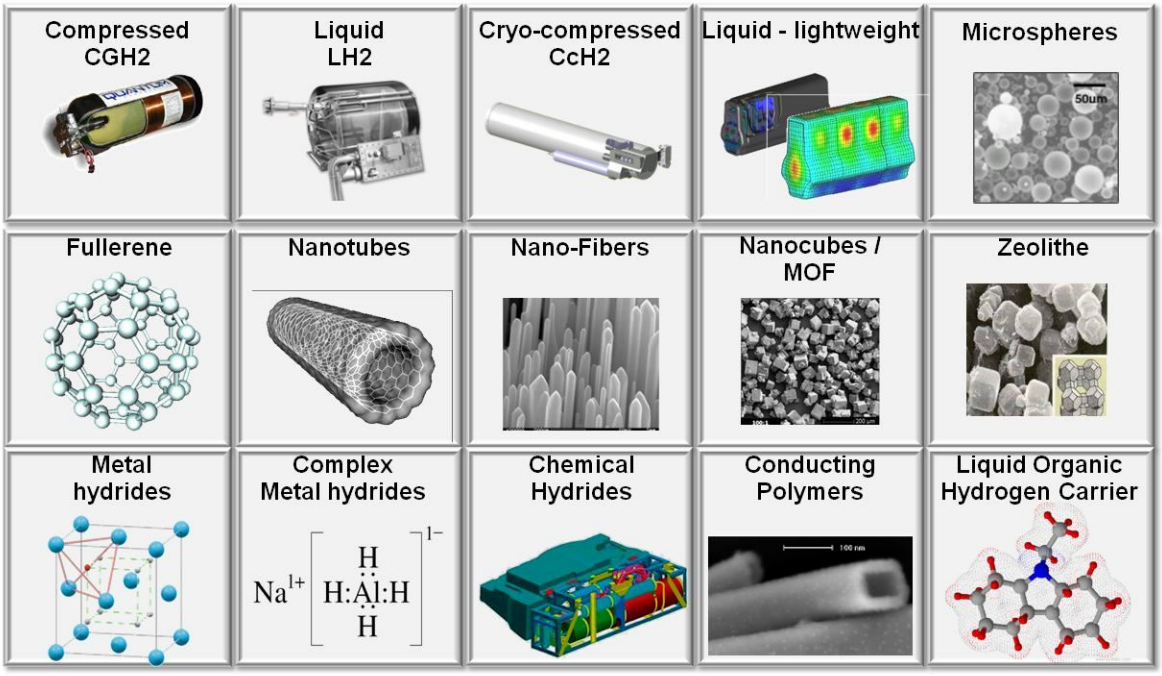

Figure 1: Overview of different hydrogen storage alternatives.

The different hydrogen storage technologies vary in the nature and strength of the hydrogen binding, measured as binding enthalpy ΔH. By using the free energy, ΔG, and the Van't Hoff equation, operation pressure and temperature and thermodynamic stability of the chemical reaction are interrelated.

This leads to the following consequences for the previously mentioned vehicle: Let's take into account an alternative storage material with a binding enthalpy of ΔH = 40 kJ / mol H_2 (e.g. Sodium Alanate). For the loading or unloading of 5 kg hydrogen, an effective thermal energy of ca. 100 MJ is involved. If the tank should be loaded with hydrogen in 3 minutes (as convenient for gasoline tanks), a thermal load of ca. 0.6 MW (!) has to be cooled through a heat exchanger during the exothermic reaction. By contrast, the unloading during full load driving conditions with the dehydrogenation rate of 9 kg H_2 / hr. requires a maximum heat load of only 50 kW. This example shows that especially the loading of alternative hydrogen storage materials with hydrogen is not an easy matter. On the one hand, the required stability of the hydrogen storage materials requires a relatively high binding enthalpy. On the other hand, a higher enthalpy demands a higher cooling power during hydrogen loading, especially if fast fueling is necessary. Against this background, the question is whether it would be a better solution to fuel fully loaded H_2 storage materials directly to the car than the onboard hydrogenation of the storage materials with the inevitable high thermal loads. Needless to say, this fueling method benefits from alternative storage materials in liquid form.

The class of so-called Liquid Organic Hydrogen Carriers (LOHC), where the carrier material is built of organic molecules, seems to be predestinated for a usage onboard of vehicles, because most of them are liquid under ambient conditions in the temperature regime of automotive applications and can be easily rehydrogenated with hydrogen. Therefore, LOHC-tank systems do not need to be insulated or pressurized and could be manufactured as free form tanks in conventional gasoline architecture. Dehydrogenation requires a reactor device, where the hydrogen-rich molecule „LQ∗H_{2x}" is separated under heat supply and in contact with a catalyst to yield a hydrogen-poor carrier material „LQ" and hydrogen:

$$LQ^*H_{2x} + \text{Heat} \rightarrow LQ + x\ H_2.$$

The separation of the functionalities „storage" and „dehydrogenation" also allows the heating of just the required amount of liquid to the reaction temperature, than warming-up the full tank system as in solid storage materials. The dehydrogenated carrier material can be stored in a two-chamber tank system and can be transported back to a centralized facility for rehydrogenation. Ideal hydrogen binding enthalpies for LOHC are between 40 and 70 kJ / mol H_2. Rehydrogenation is possible under moderate H_2 pressures (ca. 70 bar) and temperatures (ca. 150 °C) under heat dissipation.

The basic idea of hydrogen storage in organic liquids is not new [10-13]. With the obtained gravimetric and volumetric material storage density (with up to 7.2 % and 70 g H_2 / l), these LOHC have always been in the field of vision of the research engineers. However, a major issue for an automotive usage was the high temperatures necessary for the dehydrogenation of the material. Recently, new research activities at Air Products now have lead to novel LOHC materials with a significant reduction of the required operation temperature to approx. 200 °C [14]. For a further elucidation of that visionary idea, BMW Group Research and Technology has joined forces with Air Products, United Technologies Research Center (UTRC)

and Pacific Northwest National Lab (PNNL) inside the U.S. DOE-funded project “Reversible Liquid Carriers for an Integrated Production, Storage & Delivery of Hydrogen“. As mentioned, a primary need to realize the use of LOHC in practical applications is an efficient reactor system for the separation of hydrogen from the carrier. Therefore, the project focus is the setup of a reactor prototype with a hydrogen production rate of 1g H_2 / min. to demonstrate the technical feasibility. The necessary energy input, as heat, requires good heat transfer properties within the reactor. An additional challenge is the clean separation of the large amount of gaseous hydrogen generated from the LOHC (>600:1 ratio of hydrogen gas volume to liquid carrier volume at ambient temperature and 1 bar pressure).

The initial research on dehydrogenation reactors were concentrated on two types of continuous flow reactors, packed beds with pelleted catalysts and monolith structured packings. Our test compound, perhydro-N-ethylcarbazole, was dehydrogenated over a variety of pelleted catalysts, (e.g. Pd on alumina) in a packed bed. In all cases, the dehydrogenation proceeded normally, and reactor behavior was typical of a trickle bed reactor. The hydrogen purity was >99.9% even though only a simple tangential flow separator was used to isolate the gaseous product. We anticipated that packed beds would suffer from inefficiencies due to the high hydrogen gas flow rate and catalyst size. An understanding of the flow limitations was obtained by feeding hydrogen to the inlet of the reactor to simulate high gas flow rates which would be found in a full-scale reactor. The addition of hydrogen caused a “drying out” of the catalyst surface. The dry catalyst surface is not effective for reaction, and the flow of product hydrogen decreased. We anticipated a second limitation on reaction rate because of the slow diffusion of large molecules like N-ethylcarbazole through catalyst pores (i.e. intraparticle diffusion). The effectiveness factor, defined as the ratio of measured reaction rate for the catalyst particle to the rate for the catalyst with no diffusion effects, captures this effect. Our developed model for the kinetics of the reaction on micron size particles was used to predict the reaction rate with no diffusion effects. For the packed bed reactor, an effectiveness factor of about 0.08 was estimated, i.e. the rate of reaction for the pellet is only 8% of that for very small particles.

One way to reduce the diffusion effect and to increase the efficiency of the catalyst is to decrease the diameter of the particle. This was done by using a monolith, coated in its interior surfaces with a thin layer of catalyst as a continuous-flow reactor. Corrugated, 0.05 mm iron-chromium alloy foils were coated with a tightly-adhering alumina washcoat. The coated foils were then assembled to form a 400 cpsi (cells per square inch) honeycomb monolith. The desired catalytic metal was then introduced as a washcoat onto the monolith surface. Metal usage was now excellent, with effective factors > 0.5 as compared to 0.08 for the pellets. Initial studies showed that reaction rates using monoliths are diminished by high gas flow rate. Two-phase flow proceeds through four regimes as gas flow rate increases: bubbly, Taylor flow (slug flow), annular flow and gas-continuous with liquid mist. These flow effects are complicated and further data was needed to develop rational scale-up guidelines. Our flow studies showed temperature fluctuations in the flow upstream of the monolith, indicating an unstable fluid flow field. Analysis of causes of this unstable flow led to the surprising finding that there was a small amount flow out of the entrance of the monolith against the overall pressure gradient. Recent literature references show that several types of oscillations are possible when bubbles grow during flow in microchannels, and for high rates of bubble generation, alternating flow patterns both upstream and downstream, are predicted [15;16]. This alternating flow field complicates reactor design, since it affects the residence time of

the fluid in the reactor. We conclude that while microchannel reactors such as monoliths can give high conversion and selectivity, feed distribution will be important for the final design.

Since the structure of the flow field strongly affects reactor performance, an investigation of the fluid mechanics of single- and two-phase flow in a microreactor using Computational Fluid Dynamics (CFD) was undertaken. The simulation showed that using a triangular shape of the individual channels in the monolith causes areas of low flow at the vertices of the triangle, which potentially allows for gas buildup at the wall (Figure 2).

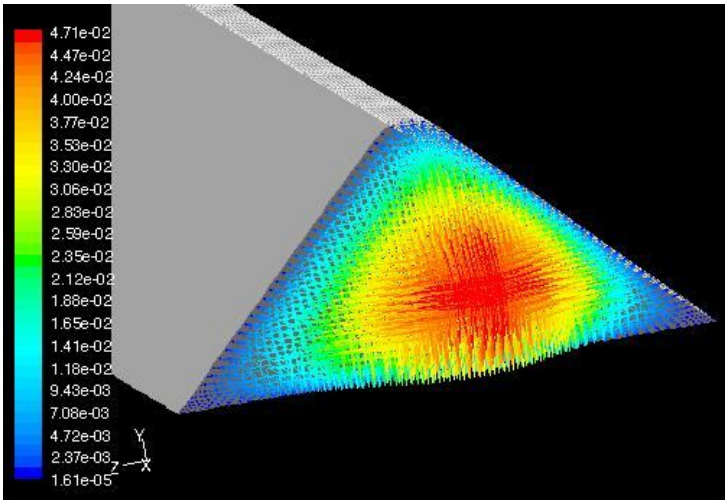

Figure 2: Computational Fluid Dynamics (CFD) simulation of velocity vectors of LOHC flow in triangular channels of a monolith reactor.

Additional work found that circular tubes have only thin layers of low flow and would be less susceptible to such buildup. The combination of high gas flow rate relative to liquid flow rate and the generation of gas at the wall results in a flow pattern in which the gas flow is along the inside of the tube wall instead of the centerline of the tube, as would be expected for the usual case of mixed gas-liquid flow entering the tube. This flow pattern seems to promote early transition to spray flow. The spray flow regime means that the concentration of liquid on the reactor walls is low. This would reduce reactor efficiency, since the liquid must be in contact with the catalyst for reaction to occur. Thus, the study shows that generation of gas at the walls of the reactor leads to novel design issues. Tube shape, catalyst distribution and gas flow pattern must all be part of the final reactor design consideration.

Microchannel reactors were considered to have design characteristics that are suitable for dehydrogenation of LOH. A microchannel reactor concept was pursued with the intent of segregating the liquid carrier from the H_2 being produced. The concept, which is illustrated in Figure 3, deploys the catalyst in a thin porous substrate that is wetting for liquid carrier and placed in a microchannel. A vapor plenum adjacent to the wick allows the H_2 to separate from the liquid as it is generated, preventing the catalyst from drying out. Proper balancing of the liquid and vapor pressures keeps the liquid in the wick by capillarity and causes the liquid to flow through the wick. This reactor concept addresses the issues of catalyst drying out and other effects of 2-phase channel flow. Experiments with the microwick reactor concept showed significantly reduced performance as indicated in Figure 3 for the wick only configuration. The test apparatus was configured to cool the vapor stream leaving the reactor caus-

ing condensation of carbazole vapors in that stream. As the liquid flow rate was decreased, more and more of the unreacted carrier was volatilized and bypassing the catalyst. To compensate, Pt/Al_2O_3 coated aluminum foam was added to the vapor channel of the wick reactor resulting in significantly improved performance, as indicated by the wick+foam data in Figure 4. However, reactor performance did not surpass performance of a packed bed of 210-420 micron particles.

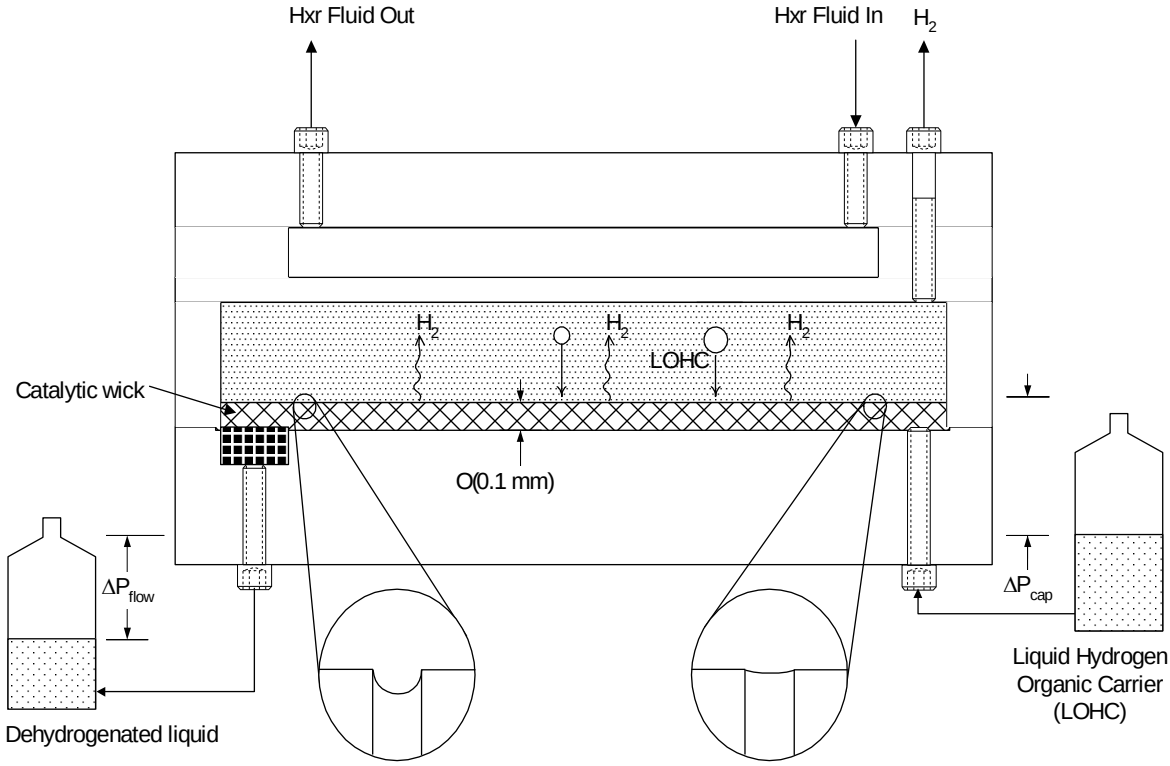

Figure 3: Microwick reactor concept for dehydrogenating a Liquid Organic Hydrogen Carrier.

The results in Figure 3 imply that phase segregation and maintaining wetted catalyst is not dictating performance in a packed bed reactor. An analysis of diffusion limitations in the packed-bed revealed that the reaction kinetics are an order of magnitude faster than the H_2 diffusion rate within the pores of the carbazole-filled catalyst particles. In addition, the kinetic rate is of the same order of magnitude as the H_2 diffusion rate through the liquid boundary layer surrounding the particles. The analysis also explains that much lower conversions from the wick reactor concept were caused by lower liquid velocities through the wicks that increased boundary layer thickness. The mass transfer analysis was further confirmed through experiments with smaller catalyst particles. Working with particles an order of magnitude smaller than the packed-bed particles has successfully improved catalyst productivity from 0.02 g H_2/g Pt/min at 90% conversion for the packed bed to 1.5 g H_2/g Pt/min, which is 75% of the original target.

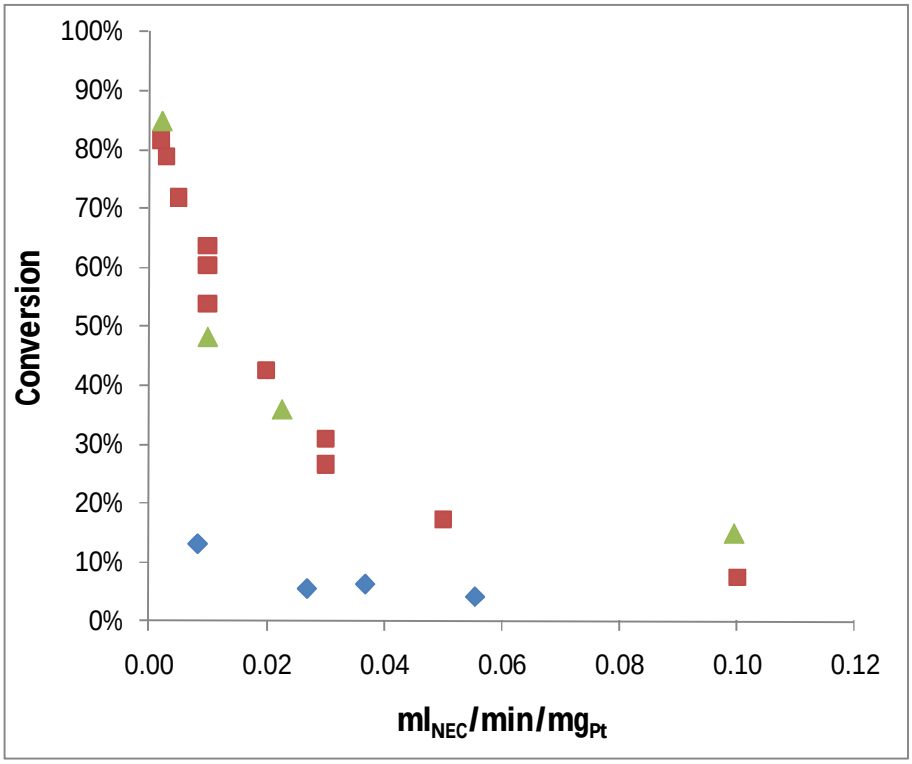

Figure 4: Conversion of n-ethyl carbazole as a function of liquid flow rate normalized by catalyst loading for a packed bed of 210-420 micron particles (■), a microwick reactor (♦), and a microwick reactor with a catalyst-loaded foam insert in the vapor space (▲).

The team is now working to realize this level of performance in a proof-of-concept reactor producing 0.1 g/min of H_2. This will be followed by a gas-heated prototype reactor capable of supplying a 1 kWe scale PEM fuel cell. If successful, the engineered catalyst volume will be less than 40 ml.

At BMW, the existing test bench to operate liquid carrier materials during dehydrogenation in microstructured reactors has been changed. Additionally, a new facility has been constructed for analysis during rehydrogenation. Regarding onboard car application, first simulation results have shown that BMW hydrogen combustion engines can offer the necessary heat quantities at temperature levels necessary for the dehydrogenation of LOHCs. Therefore, an application of LOHC-storage system in a hydrogen combustion engine propelled vehicle is in principle possible.

Usage of Liquid Organic Hydrides shows a relatively simply way for the entire distribution, storage and usage of hydrogen in vehicles. The handling procedure would be, as depicted in Figure 5 largely comparable to today's usage of gasoline or diesel fuels.

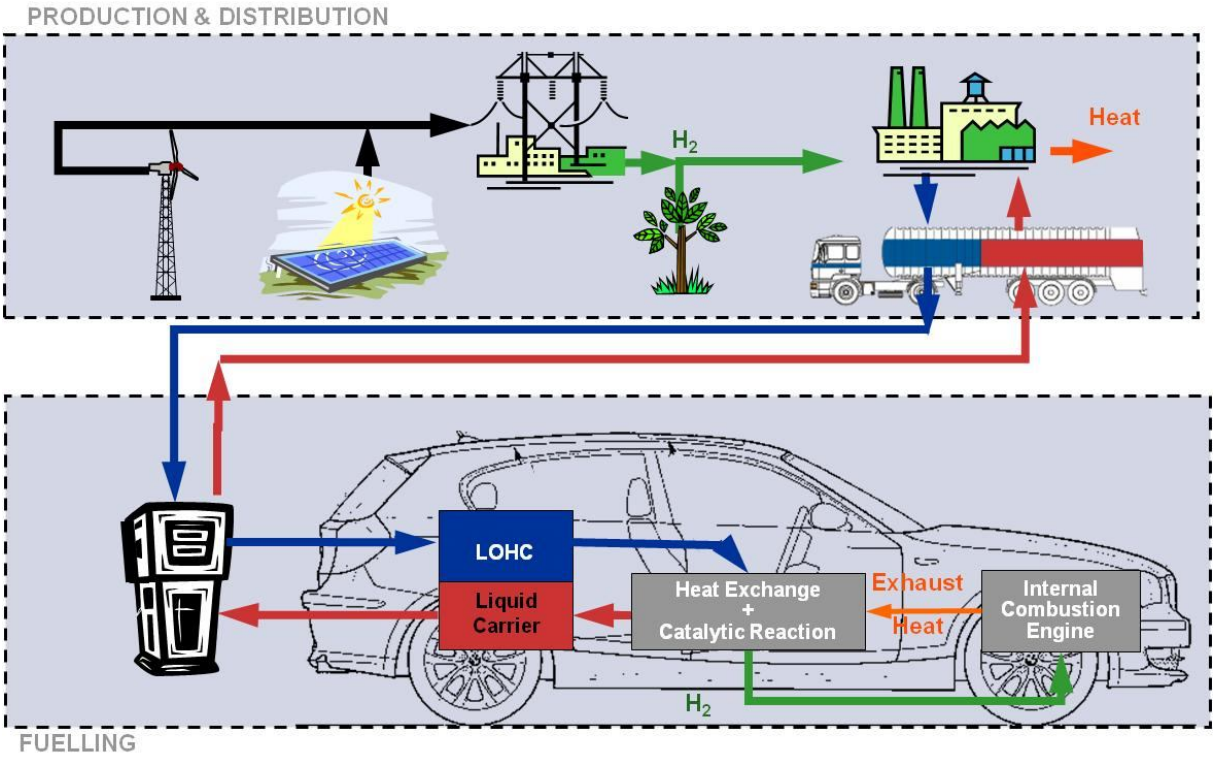

Figure 5: Vision of Liquid Organic Hydrogen Carriers in a Hydrogen based alternative energy economics.

3 Conclusion

Liquid Organic Hydrogen Carriers (LOHC) are liquid pumpable, easily rechargeable and have, at acceptable gravimetric storage densities, similar volumetric storage densities than cryogenic liquid hydrogen.

The off-board recycled fuel can be stored and transported at ambient conditions and does not need an entirely new filling station infrastructure.

Inside the above mentioned DOE-funded project, we are striving to make that vision reality.

The Authors would like to thank the Department of Energy for financial support through contract #DE-FC36-05GO15015.

References

[1] Freymann, R., Pehr, K, Strobl, W. : Twenty-five Years of Continuous Hydrogen Research at BMW. JSAE Paper Number 20025305. Proceedings of the JSAE Annual Congress, Yokohama, Japan (2002).

[2] Strobl, W. : BMW H2R. NHA Annual Hydrogen Conference, Washington, D.C., USA (2005).

[3] Fickel, HC, Heller, K, Kresse, T, von Wild, J.: Ist der Wasserstoffverbrennungsmotor schon auf der Überholspur? 6. Dresdner Motorenkolloquium (2005).

[4] Freymann, R., Strobl, W, Kübler, J. : Wasserstofftechnologie im Automobilbau: nachhaltig, sauber, leistungsfähig. Erste Österreichische Wasserstoff-Konferenz, Graz (2005).

[5] The BMW Hydrogen 7. Available at: http://www.bmw.com/com/en/insights/technology/efficient_dynamics/phase_2/clean_energy/bmw_hydrogen_7.html;. Accessed 01.09.2008.

[6] Danner, S., Fürst, S. : BMW Hydrogen 7 series - a safe way to a clean future. FISITA, Yokohama, Japan (2007).

[7] Fürst, S, Gräter, A, Pehr, K.: Hydrogen 7: The First Premium Saloon with a Bivalent Internal Combustion Engine. JSAE Paper Number 20075338. JSAE Proceedings 28, 5-8 (2007).

[8] von Wild, J., Freymann, R, Zenner, M. : Potentiale von alternativen Wasserstoff-Speicherungstechnologien. VDI-Berichte: Innovative Fahrzeugantriebe 2008, Dresden/Germany , 2030, 273-298 (2008).

[9] Aceves, SM, Espinosa-Loza, F, Ledesma-Orozco, E, Ross, TO, Weisberg, AH, Brunner, TC, Kircher, O.: High-density automotive hydrogen storage with cryogenic capable pressure vessels. Int J Hydrogen Energy 35, 1219-1226 (2010).

[10] Scherer, GWH, Newson, E.: Analysis of the seasonal energy storage of hydrogen in liquid organic hydrides. International Journal of Hydrogen Energy 23, 19-25 (1998).

[11] Taube, M, Rippin, D, Knecht, W, Hakimifard, D, Milisavljevic, B, Gruenenfelder, N.: A prototype truck powered by hydrogen from organic liquid hydrides. International Journal of Hydrogen Energy 10, 595-599 (1985).

[12] Hodoshima, S, Arai, H, Takaiwa, S, Saito, Y.: Catalytic decalin dehydrogenation/naphthalene hydrogenation pair as a hydrogen source for fuel-cell vehicle. International Journal of Hydrogen Energy 28, 1255-1262 (2003).

[13] Kariya, N, Fukuoka, A, Ichikawa, M.: Efficient evolution of hydrogen from liquid cycloalkanes over Pt-containing catalysts supported on active carbons under "wet-dry multiphase conditions". Applied Catalysis A: General 233, 91-102 (2002).

[14] Pez, G, Scott, A, Cooper, A, Cheng, H, Bagzis, L, Appleby, J, inventor: HYDROGEN STORAGE REVERSIBLE HYDROGENATED OF PI-CONJUGATED SUBSTRATES. patent WO 2005/000457 A2. 06.01.2005 (2005).

[15] Xu, J, Feng, Y, Cen, J.: Transient flow patterns and bubble slug lengths in parallel microchannels with oxygen gas bubbles produced by catalytic chemical reactions. Int J Heat Mass Transfer 50, 857-871 (2007).

[16] Wang, G, Cheng, P, Wu, H.: Unstable and stable flow boiling in parallel microchannels and in a single microchannel. Int J Heat Mass Transfer 50, 4297-4310 (2007).